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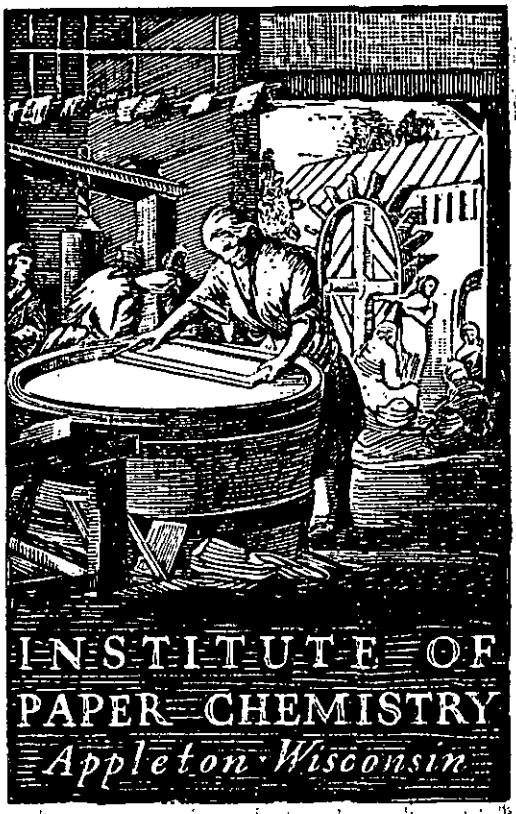

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

CHEMISTRY OF HOLOLIGNIN

Research Grant

Project 2500

Report Four

A Progress Report

to

The Grantors

ALBEMARLE PAPER COMPANY
KIMBERLY-CLARK CORPORATION
SCOTT PAPER COMPANY
UNION CAMP CORPORATION
WEST VIRGINIA PULP AND PAPER COMPANY

January 16, 1968

THE INSTITUTE OF PAPER CHEMISTRY

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SUMMARY

This report is a continuation of the hololignin study which was initiated in Progress Report Two. The new results confirm the suggestion that the reaction of chlorine dioxide or acidified chlorite with wood converts the lignin to a wide range of degradation products. It now seems that the proportion of the various degraded lignins depends on the amount of oxidant used.

With chlorite equivalent to slightly more than 100% chlorine dioxide, some carbohydrates are dissolved in the spent liquors and some are degraded to materials which are soluble in acetone after alkaline extraction. When the amount of oxidant is equivalent to 18% or less chlorine dioxide, as in the usual holopulping, lignin in the interior of the chips may be modified considerably without loosening the bonds which retain the lignin in the wood and hold the fibers together. Part of the modified, residual lignin can be extracted easily with sodium hydroxide, suggesting that one of the main functions of chlorine dioxide may be to convert lignin to a form that can be extracted in a second stage. However, some lignin is quite resistant to chlorine dioxide oxidation-alkaline extraction, and more than two stages seem necessary for the preparation of holopulps.

The procedure suggested in Report Two for estimating lignins in holopulps is not satisfactory when only 6% chlorine dioxide is reacted with wood because a considerable part of the lignin extractable with sodium hydroxide is not soluble in dry acetone. Preliminary experiments with pinewood indicate that pine hololignins can be isolated and characterized.

INTRODUCTION

The Institute is engaged in the development of a holopulping process in which wood is reacted with selective delignifying agents in a manner designed to produce high-yield pulps. The development is hindered by the very limited understanding of the nature of the changes which occur when wood is reacted with chlorine dioxide or acidified chlorite, and by the lack of a reliable means of estimating lignin in the holopulps. Progress Report Two described work which was directed toward an increased knowledge of the reactions which occur in holopulping, and toward the development of better means of estimating lignins in the resulting pulps. The present report is a continuation of this work.

A brief summary of the reactions of model compounds given in Appendix I of Progress Report One suggests that chlorine dioxide may react with lignin in several different ways, including chlorination, demethoxylation, oxidation to quinone structures, displacement of C-3 chains, and oxidative cleavage of aromatic ring structures. However, the relative contribution of these different reactions to holopulping has not been determined.

Results given in Progress Report Two showed that the reaction of acidified chlorite with aspenwood converts part of the lignin to materials soluble in the spent chlorite liquor, and part to materials which can be extracted from the reacted wood with dilute sodium hydroxide solutions. Much of the alkali-extracted hololignins is soluble in acetone and can be separated from hemicelluloses and from the sodium chloride produced on acidification of the alkaline extract. These acetone-soluble hololignins cannot be extracted with acetone directly from the reacted wood. Hence, the alkali treatment seems to cause some fission of the lignin polymer, or of a lignin-carbohydrate linkage.

Attempted isolation of hololignins from the spent chlorite liquors were not very satisfactory, but acetone-soluble hololignins were isolated with ease from the reacted wood. These isolated hololignins were degradation products in that they were partially chlorinated, oxidized, and demethoxylated. They retained some aromatic character, but much of this character had been lost.

The determination of lignin in holopulps and holocelluloses is very uncertain because an appreciable part of the lignin has been degraded to the point where it is soluble in the Klason lignin filtrate. Since the absorptivity of the degraded lignin is low and variable, estimation of the acid-soluble lignin from ultraviolet absorbance is only a rough approximation. In the previous work it was suggested that the best estimate of the lignin content might be the sum of the isolated acetone-soluble hololignin and the Klason lignin plus acid-soluble lignin remaining in the pulp after the alkaline treatment used to extract the acetone-soluble hololignin. This procedure was designated modified lignin analysis in Tables IV and XIX in Progress Report Three.

EXPERIMENTAL RESULTS

TERMINOLOGY AND GENERAL PROCEDURES

In Progress Report Two the wood residue obtained by treating wood with acidified chlorite was called pulp, and the residue remaining after alkaline extraction to remove hololignin was designated residual pulp. This terminology is not very satisfactory because the so-called pulp is not a true pulp, and because caustic extraction is normally used to produce pulps in the work on the development of a holopulping process.

The terminology used in the present report is as follows: The product obtained by reacting wood with acidified chlorite or chlorine dioxide is designated "reacted wood" rather than pulp as was done previously. After extracting the reacted wood with sodium hydroxide to remove hololignins, the residue is designated "residual reacted wood" rather than residual pulp. The term hololignin is used in a broad sense to designate the various degraded lignins.

Distilled water and reagent-grade chemicals and solvents were used but the sodium chlorite was technical grade and ether extractions were made with U.S.P. ether. Acetone was redistilled to remove nonvolatile constituents. All solutions were evaporated under reduced pressure at temperatures of 40°C. or less. Moisture tests were made by oven drying overnight at 100-105°C. Isolated hololignins were dried in a vacuum desiccator containing calcium chloride, sodium hydroxide, and sulfuric acid. Samples for analysis and the residual reacted wood samples were dried in a vacuum desiccator containing phosphorus pentoxide.

Hololignins were isolated by treating the reacted wood with 0.5N sodium hydroxide for three hours at room temperature under nitrogen, acidifying with a

slight excess of 3N hydrochloric acid, adding acetone (9 volumes per volume of aqueous solution), filtering, and washing with 90% acetone. The filtrate combined with the washings was evaporated to dryness, and the residue was extracted with acetone to give an acetone-soluble fraction. In some instances the fractions were subdivided further by solubility in different solvents or by dialysis, and in some cases the acetone-insoluble residue was extracted with 90% acetone to yield additional lignin material.

Total chlorine was determined by the Schöniger procedure for combustion and the Volhard procedure for titration. Water-soluble chlorides were determined by suspending the sample in water, centrifuging, and then titrating in the usual manner. Carbon and hydrogen were determined by combustion, and oxygen was estimated by the Unterzaucher method. Methoxyl was determined by Institute Method 18. For the acid numbers, 50-mg. samples dissolved in 150 ml. of ethanol-water 1:1 were titrated conductometrically with 0.05N sodium hydroxide in the same solvent. In each case, there were two inflection points in the titration curve, the first being similar to that produced when strong acids are titrated. Acid No. I was calculated from the titration to the first inflection point, whereas Acid No. II was calculated from the difference between the total titration and the titration to the first inflection. In Progress Report Two, Acid No. II in Table III was calculated from the total titration, and thus corresponds to the sum of Acid No. I and Acid No. II as calculated in the present report.

Infrared spectra were determined by the potassium bromide pellet technique, and ultraviolet spectra were determined on aqueous ethanol solutions using the Carey Model 15 Spectrophotometer.

Klason lignin was determined by Institute Method 428. Acid-soluble lignin values were calculated from the absorbance at 208 nm. using a standard absorptivity of 105 for lignin at this wavelength (2,3). Since the absorptivity of the hololignins at 208 nm. is often much less than 105, the acid-soluble lignin values are believed to be low.

Chlorine dioxide consumption tests were made by adding 10 ml. of water to 50 mg. of hololignin in a 1-ounce narrow-mouth, screw cap bottle, precooling in a refrigerator, and then adding 10 ml. of freshly prepared solution containing 55 to 60 mg. of chlorine dioxide. The bottle was tightly sealed using a 4-mil sheet of polyethylene under the screw cap, and then was heated for 4 hours in a water bath at 55-60°C. After heating, the bottle was cooled in the refrigerator for two hours, and then the cold mixture was transferred to a flask containing potassium iodide for titration by the procedure described on pages 771-2 in the TAPPI Monograph on bleaching (5). Since the neutral titration was uncertain in some cases, and since the chlorine concentration was only about 1 part per 100 parts of chlorine dioxide, the results given in this report were calculated from the total titration without any correction for the small amount of chlorine which was present in all cases. Chlorine dioxide consumption expressed as percentage of the hololignin weight was calculated from the difference in the final concentration and that present in a control run at the same time. Under the conditions used, the chlorine dioxide loss in the controls was approximately 10%.

ADDITIONAL MATERIAL EXTRACTED WITH HOT ALKALI

In Progress Report Two, hololignins were often extracted from reacted wood[1] with hot sodium hydroxide. However, for a wood which had been reacted with large

[1] See previous section for terminology.

amounts of acidified chlorite over an extended period, the yield of acetone-soluble material seemed higher than the likely lignin content, suggesting that the hot alkali had extracted acetone-soluble materials of nonlignin origin. The scheme outlined in Fig. 1 was carried out to isolate some of the materials extracted with hot alkali which were not removed by room temperature extraction.

Two chloritings were made at 50°C. the first being completed in 8 hours, but the second covered a one-week period with a total heating time of 50 hours. The low yield of the reacted wood indicates that some carbohydrate material in addition to lignin was dissolved by the extensive chloriting. The conditions were selected to produce large amounts of the additional materials extracted with hot alkali, and are not representative of those used in holopulping or even for the preparation of holocellulose.

The original acetone-soluble fractions from both the room temperature and the hot alkali extractions were extracted nine times with U.S.P. ether. Evaporation of the combined ether solutions gave a fraction which was not completely soluble in small amounts of ether, but in this report it is designated the ether-soluble fraction.

The reacted wood and the two residual reacted woods were essentially free of Klason lignin. The calculated acid-soluble lignin contents were: reacted wood 0.62%, residual reacted wood from the room temperature extraction 0.16%, and residual reacted wood from the hot alkali extraction 0.14%.

Infrared spectra for the fractions from the room temperature extractions are given in Fig. 2, and spectra for the fractions from the hot extraction are presented in Fig. 3. All of the spectra show strong hydroxyl and carbonyl stretching bands in the 3400 $cm.^{-1}$ and 1730 $cm.^{-1}$ regions, respectively. The spectra for the three fractions from the room temperature extraction have a shoulder at about 1510 $cm.^{-1}$ indicating

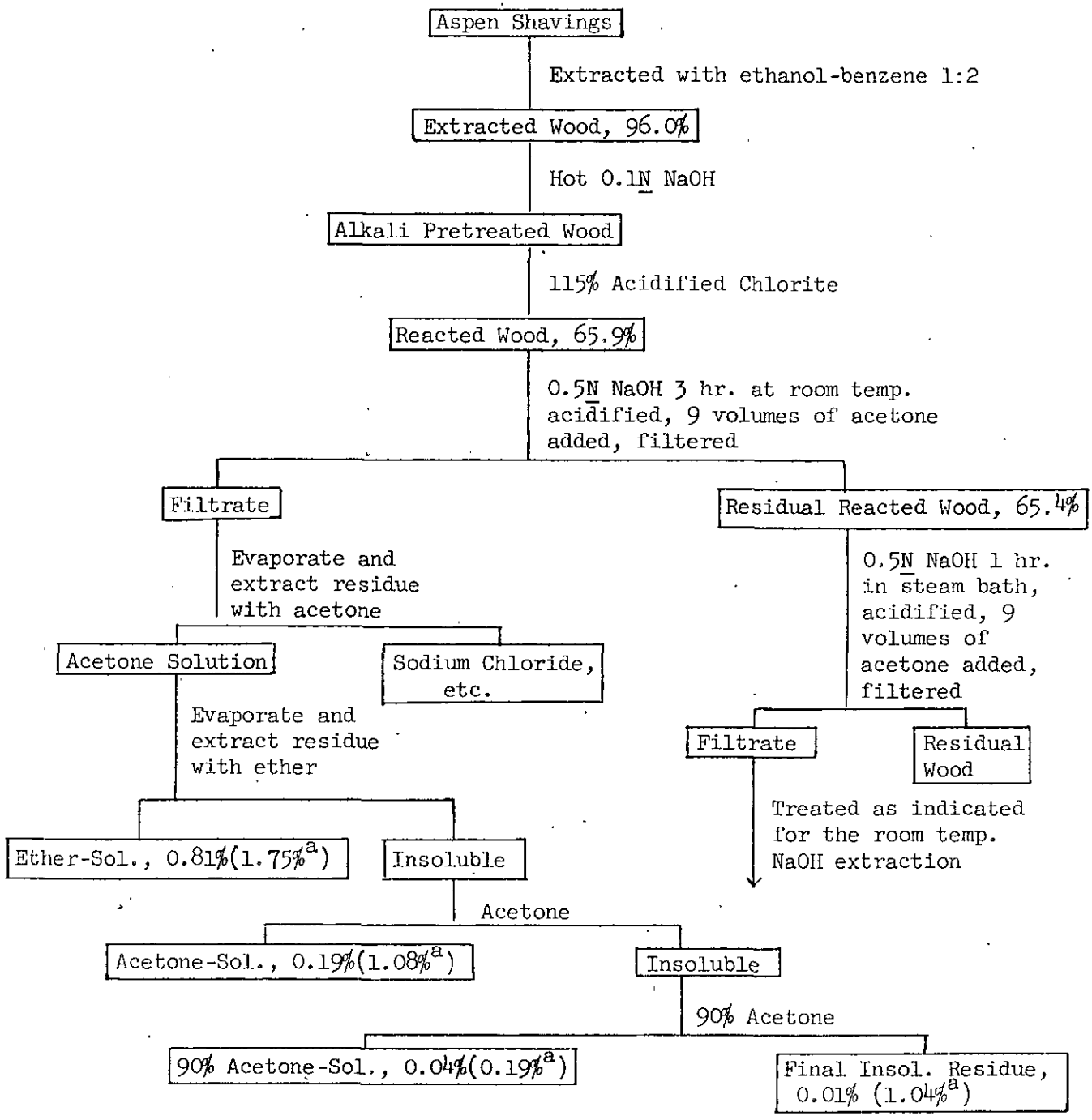

Figure 1. Isolation of Hot Alkali Extracted Materials (Percentages are Based on Original Aspen Shavings)

[a]Yield of material from the hot NaOH extraction.

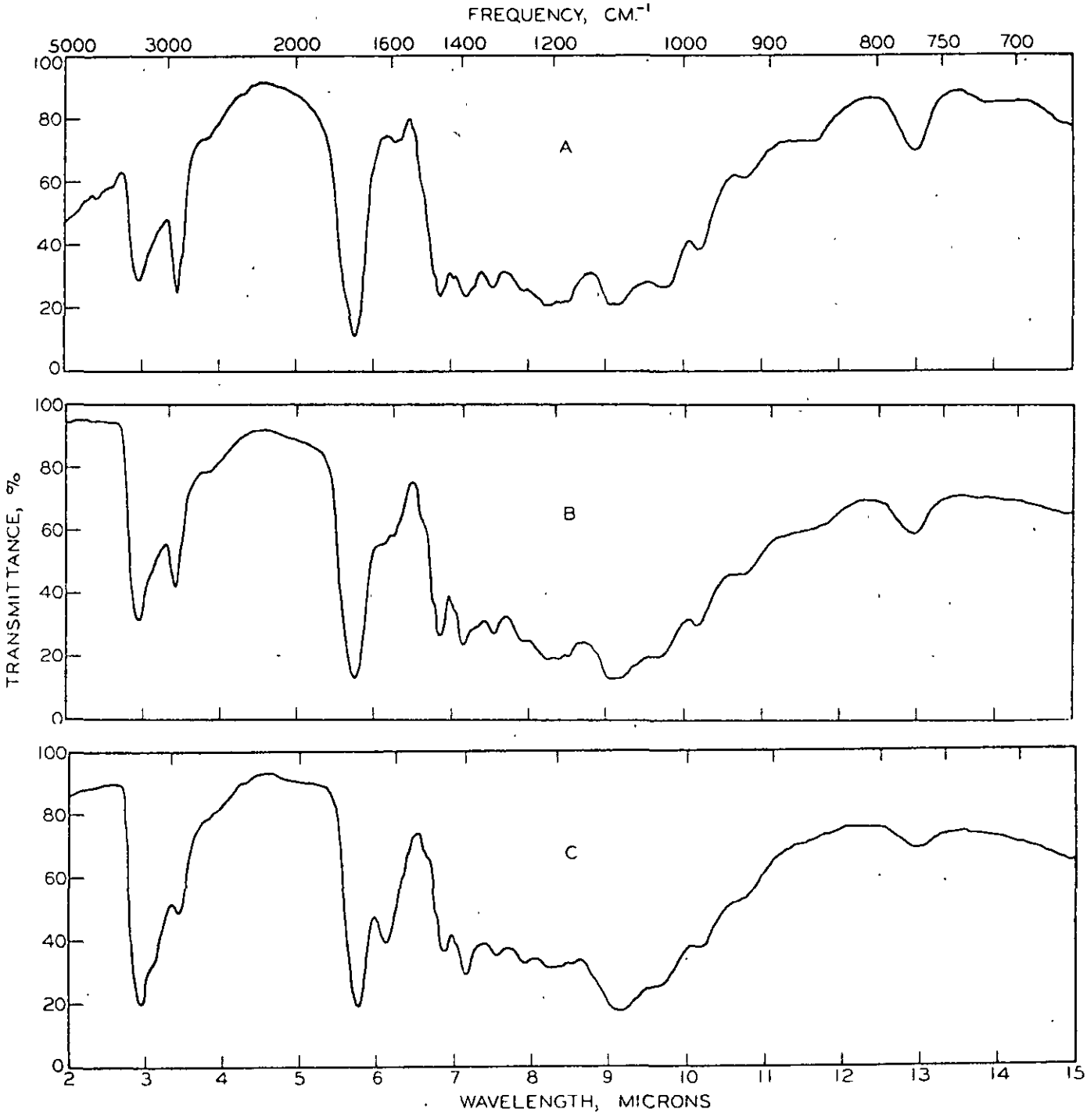

Figure 2. Infrared Spectra of Fractions from Room Temperature Extraction

A = Ether-soluble
B = Acetone-soluble
C = 90% Acetone-soluble

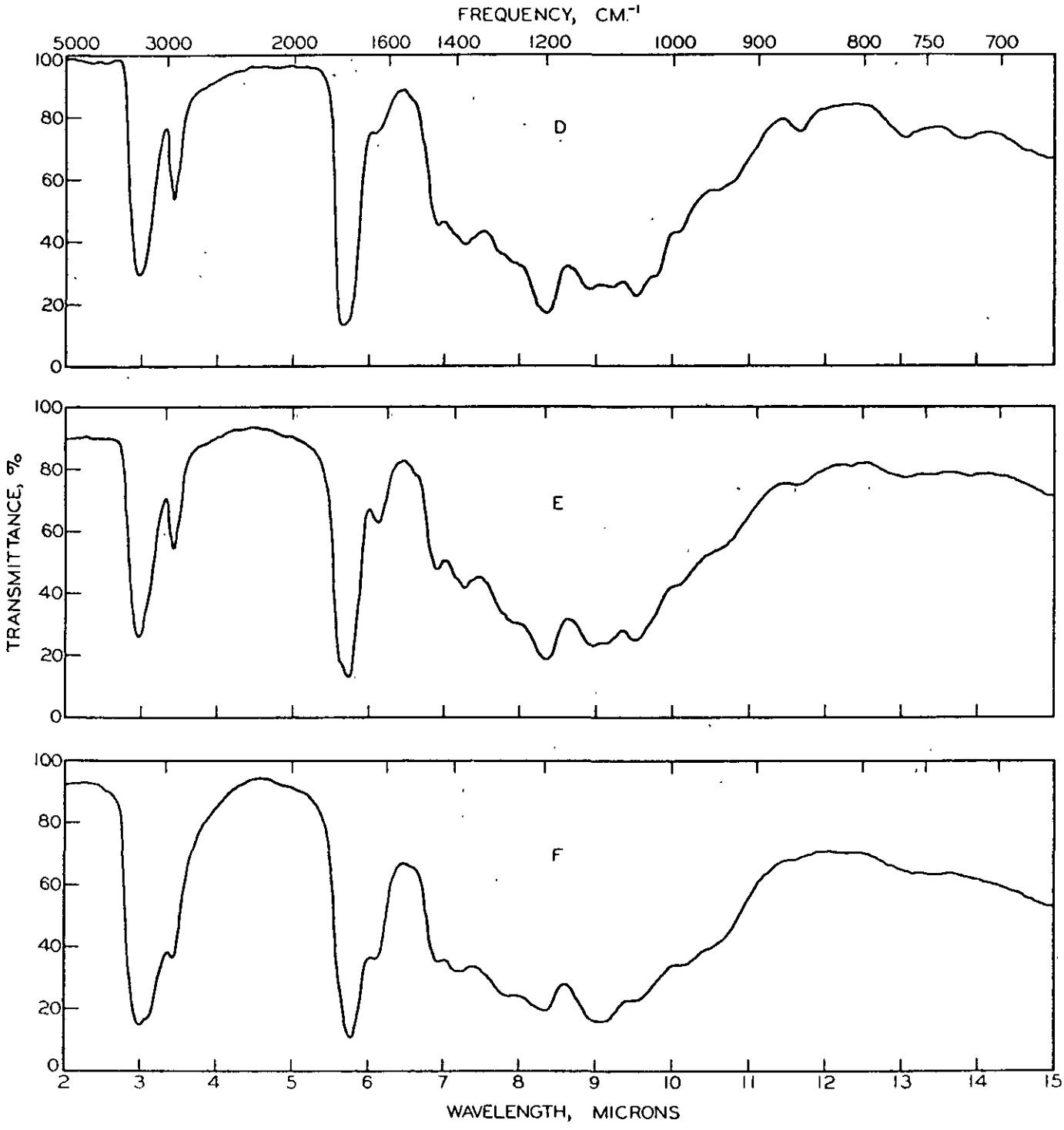

Figure 3. Infrared Spectra of Fractions from Hot Alkali Extraction

D = Ether-soluble
E = Acetone-soluble
F = 90% Acetone-soluble

aromatic C=C stretching vibrations (1). On the other hand, the spectra in Fig. 3 for the fractions from the hot extraction fail to provide any clear indication of aromatic character.

Ultraviolet absorptivities for the six fractions are given in Table I. Absorptivities for a milled wood lignin are included for comparison. These were calculated from data given in Busche's thesis for milled wood lignin A (2). (In Table I of Progress Report Two, the absorptivities for a milled wood lignin were calculated from Busche's data for milled wood lignin RT.) The fractions from the room temperature extraction have ultraviolet spectra somewhat similar to the spectrum of milled wood lignin from aspen. The maximum near 210 nm. occurs at a slightly lower wavelength in the hololignins, and their absorptivity is generally less than half that of the milled wood lignin. The fractions from the hot extraction have very low absorptivity at 212 nm. and shorter wavelengths, but in the range of 260 to 300 nm. the absorptivity of the fractions from the hot extraction are nearly equal to that of the corresponding fractions from the room temperature extraction.

PENETRATION OF CHLORITE LIQUOR

When aspen chips are reacted with acidified chlorite equivalent to 18% chlorine dioxide, only the outside of the chips are softened to the point where individual fibers are formed by mild mechanical action. Initially, it was believed that lack of penetration of chlorite liquor may have been responsible for the poor pulping action in the interior of the chips. To investigate this the hard centers of reacted chips were compared with fibers from the outside of the reacted chips.

Figure 4 outlines the preparation of the two fractions along with an intermediate fiber bundle fraction which was not investigated. The chlorite reacted chips were stirred with water in a Waring Blendor before the Bauer McNett separation.

The hard centers were retained on both the 20- and 12-mesh screens, whereas the fibers passed the 20-mesh screen and mostly passed the 35-mesh screen. The fibers were retained on the 65-mesh screen. There was a considerable mechanical loss in the separation.

TABLE I

ULTRAVIOLET ABSORPTIVITY OF EXTRACTED FRACTIONS

Wavelength, nm.	Room Temp. Extraction[a] A	B	C	Hot Extraction[a] D	E	F	MWL-A[b]
206	45.0	55.9	46.7	6.2	9.7	12.4	--
207	44.4	57.2	46.8	6.0	9.4	12.1	--
208	44.9	56.8	46.7	5.9	9.1	12.0	--
209	44.4	56.8	45.4	5.4	8.8	11.6	60.0
210	44.2	55.9	45.6	5.4	8.7	11.4	79.5
211	43.0	54.5	44.8	5.3	8.7	11.1	91.7
212	42.0	53.8	43.2	5.2	8.4	10.5	98.0[c]
230	18.5	23.4	19.3	4.4	6.9	9.0	38.4
240	12.3	15.7	13.3	3.9	6.3	7.4	31.0
250	6.9	8.7	7.6	3.8	6.0	7.0	17.5
260	4.7	6.0	5.7	3.7	5.9	6.9	13.5
270	3.7	5.2	5.2	3.3	5.2	6.4	13.9
280	2.9	4.9	5.0	2.9	4.1	5.5	13.2
290	2.1	4.2	4.2	2.4	3.2	4.7	8.6
300	1.6	2.8	3.0	1.4	2.7	4.0	5.4

[a] A and D = Ether-soluble fractions, B and E = acetone-soluble fractions, C and F = 90% acetone-soluble fractions.
[b] Calculated from data in Busche's thesis.
[c] Maximum at 212.5 nm.

The hard centers were ground in an Abbé mill. Both the ground material and the fibers were analyzed for chlorine and for lignin by the modified procedure. In addition, the isolated acetone-soluble hololignins were analyzed for methoxyl, total chlorine, and water-soluble chlorides.

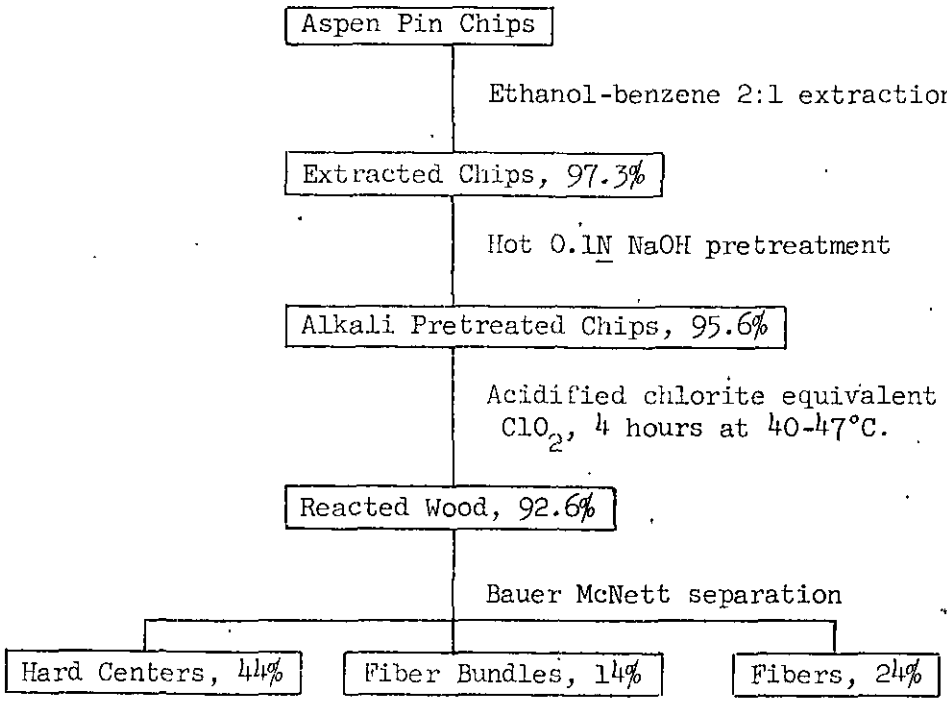

Figure 4. Separation of Fibers from Hard Chip Centers (Percentages are Based on Original Pin Chips)

The results in Table II show that the hard centers contain more lignin than he fibers, but the difference is surprisingly small. The data fail to indicate any lear difference in the composition of the hololignins isolated from the two fractions. ence, it seems that the difficulty in pulping the center of the chips is not due en- irely to poor penetration.

The calculated chlorine to lignin ratios in Table II are higher than the ctual chlorine contents of the isolated hololignins. This suggests that either some hlorine is lost in the alkaline extraction or that the total lignin values are low. he latter possibility seems likely. The lignin content of the wood before chloriting as not determined, but it seems likely that alkali-pretreated wood contained approxi- ately 22.6% lignin as was reported on page 28 of Progress Report Two for a similar retreated wood. On this basis and based on the high yield, it seems likely that the otal reacted wood in the present study contained 18% or slightly more lignin. If the

lignin in the two reacted wood fractions contains an average of about 7.6% chlorine (as the data for the isolated lignins suggest), the lignin content can be calculated from the chlorine contents. Such a calculation indicates 17.6% lignin in the hard centers and 14.2% in the fibers. The lower values for total lignin in Table II are believed to be due to lignins which were extracted with sodium hydroxide, but which were not soluble in acetone.

TABLE II

COMPARISON OF HARD CENTERS WITH FIBERS

(Results expressed as percentage of sample)

	Hard Centers	Fibers
Reacted wood:		
Chlorine, %	1.34	1.08
Acetone-sol. hololignin, %	11.8	9.2
Klason lignin, %	0.4	0.9
Acid-sol. lignin, %	1.8	2.1
Total "modified" lignin, %	14.0	12.2
100 (Ratio chlorine/lignin)	9.6	8.9
Isolated hololignin:		
Methoxyl, %	13.8	14.5
Total chlorine, %	7.45, 7.87	7.64, 7.64
Water-sol. chlorides, %	0.19	0.26
Bound chlorine (by difference), %	7.3-7.7	7.4
Mol. ratio chlorine/methoxyl	0.46-0.48	0.45

HOLOLIGNINS FROM FIBERIZED ASPENWOOD

During the course of this study the holopulping process had been developed to the point where aspenwood was first fiberized in the Bauer, and then was reacted with 6 to 9% chlorine dioxide followed by extraction with caustic. It seemed worthwhile to investigate the hololignins produced by such a procedure.

Fiberized aspenwood prepared by passing steamed chips through the Bauer as described in Progress Report Three was first extracted with moist acetone to remove the extractives. The extract amounted to 4.2% of the original fiber. Three portions of the extracted fiber were reacted with 6, 9, and 18% chlorine dioxide, respectively, the amount of chemical being based on the acetone-extracted fiberized wood. In each case, the pH of the initial chlorine dioxide solution was adjusted to the range 6.8 to 7.3 by addition of sodium hydroxide. The chlorine dioxide solutions were prepared from sodium chlorate and oxalic acid (4), and about 1% of the active oxidant consisted of chlorine. The reaction mixtures were kept in the dark at room temperature until the chlorine dioxide was exhausted. The pH of the spent liquors was 2.6, 2.4, and 1.9 for the 6, 9, and 18% reactions, respectively.

Hololignins were isolated from the three spent liquors and from the three reacted wood samples by the scheme shown in Fig. 5, and the yields are given in Tables III and IV. There was no evidence of secondary reactions in the recovery of hololignins from the spent liquors, as was observed previously in the spent chlorite liquors.

It was expected that a considerable part of the hololignins in the spent liquors would be soluble in ether because of extensive degradation. Consequently, an ether-soluble fraction was isolated first from the spent liquors, but the yield of this fraction was quite small. Since an appreciable part of the spent liquor solids was insoluble in acetone, both a 90% acetone-soluble fraction and the insoluble residue were

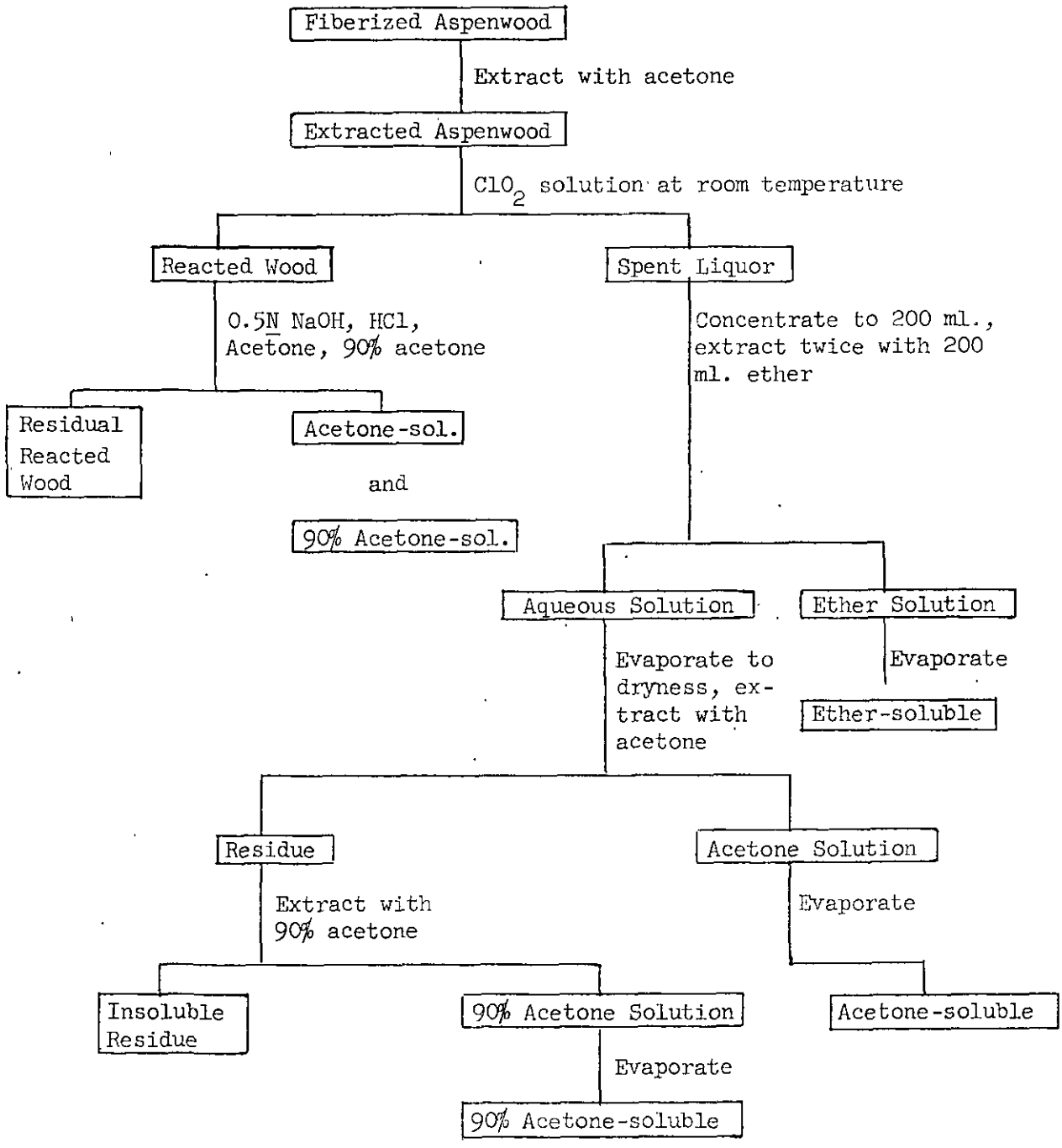

Figure 5. Isolation of Hololignins from Fiberized Aspenwood

isolated. The weight of insoluble residue was corrected for sodium chloride by assuming that the sodium hydroxide added to the original liquor had been converted to sodium chloride and that this was present in this fraction.

TABLE III

REACTED WOOD BEFORE AND AFTER ALKALINE EXTRACTION

	Reacted Wood			Residual Reacted Wood		
	6% ClO_2	9% ClO_2	18% ClO_2	6% ClO_2	9% ClO_2	18% ClO_2
Yield[a], %	92.2	90.3	81.7	75.8	69.0	69.0
Analytical data:[b]						
Chlorine, %	0.7	0.8	1.0	0.2	0.2	0.3
Klason lignin, %	17.0	14.0	7.2	9.8	6.4	3.7
Acid-sol. lignin, %	5.7	6.5	6.4	2.0	2.0	1.6
Klason plus acid-sol. lignin, %	22.7	20.5	13.6	11.8	8.4	5.3
Modified lignin[c], %	19.7	21.7	17.6	--	--	--

[a] Based on original fiberized aspenwood.
[b] Based on sample.
[c] (Acetone-soluble hololignin isolated from reacted wood) + (Klason and acid-soluble lignin in residual reacted wood), both based on reacted wood.

For the reactions with 6 and 9% chlorine dioxide, the yields of extractives, hololignins from the spent liquor, and the reacted wood total slightly more than 100%, although on a chlorine-free basis the summations are slightly less than 100%. Thus, the yields for these two reactions account for nearly all of the reaction products. On the other hand, the yields for the reaction with 18% chlorine dioxide fail to account for 8% or more of the reaction products. This may be due in part to the formation of volatile products, but it seems likely that some of the yield values reported for this reaction are in error.

TABLE IV

ISOLATED HOLOLIGNINS

	From Spent Liquor			From Reacted Wood			
	6% ClO_2	9% ClO_2	18% ClO_2	6% ClO_2		9% ClO_2	18% ClO_2
				I[a]	II[b]		
Yield:[c]							
Ether-soluble, %	0.2	0.3	0.8	--	--	--	--
Acetone-soluble, %	1.7	3.1	4.8	9.2	--	13.8	10.7
90% Acetone-soluble, %	0.3	0.5	0.6	5.9	1.9	3.4	0.9
Insoluble residue, %	2.2	2.1	0.0	--	--	--	--
Total	4.4	6.0	6.2	15.1	--	17.2	11.6
Analytical data for acetone-soluble hololignin:[d]							
Chlorine, %	18.5	16.5	17.6	3.6	3.2	5.0	6.2
Carbon, %	--	37.3	--	--	55.5	52.9	--
Hydrogen, %	--	3.94	--	--	5.78	5.39	--
Oxygen, %	--	40.2	--	--	33.8	36.2	--
Residue, %	--	1.45	--	--	0.0	0.99	--
Total	--	99.4	--	--	98.3	100.5	--
Methoxyl, %	6.1	4.3	4.3	15.4	19.7	15.3	10.5
Acid No. I[e]	85	90	76	38	17	39	51
Acid No. II[f]	264	278	268	114	55	101	158
ClO_2 consumption for acetone-soluble hololignin, %:[g]	24	25	16	65	--	65	61

[a] Data for the acetone-soluble product.
[b] Data for the dialyzed product from the 90% acetone-soluble fraction.
[c] Based on original fiberized aspenwood.
[d] Based on sample.
[e] Milligrams of KOH per gram of sample for first inflection point.
[f] Milligrams of KOH per gram of sample for difference between first and second inflection points.
[g] $100 \left(\frac{\text{weight of } ClO_2 \text{ consumed}}{\text{weight of sample}}\right)$.

The yield of acetone-soluble hololignin from the 6% reacted wood was less than expected, and therefore a 90% acetone-soluble fraction was isolated from the acetone-insoluble residue. A duplicate isolation of acetone-soluble and 90% acetone-soluble hololignins from the 6% reacted wood give results in agreement with those reported in Table IV. Thus, only about 60% of the hololignin extracted from the 6% reacted wood was soluble in acetone. In contrast, over 90% of the hololignin extracted from the 18% reacted wood was acetone soluble.

The 90% acetone-soluble fractions probably contain small amounts of sodium chloride. To remove this, the 90% acetone-soluble fractions from the 6% reacted wood were suspended in aqueous acetone containing a small amount of hydrochloric acid, and were dialyzed against distilled water. Material which passed through the dialysis bag amounted to 34% of the original 90% acetone-soluble fractions, and water-soluble material remaining in the bag amounted to 2%. These two fractions were not investigated, but they probably contained degraded lignins as well as sodium chloride. A 90% acetone-soluble fraction was isolated from the water-insoluble residue remaining in the dialysis bag. This fraction amounted to 34% of the original 90% acetone-soluble fraction and 19% of the original fiberized aspenwood.

In addition, part of the water-insoluble material remaining in the dialysis bag was insoluble in 90% acetone. This residue which amounted to 19% was not investigated. In this dialysis experiment, 11% of the material was unaccounted for.

Duplicate analyses indicated that the acetone-extracted fiberized aspenwood contained 22.7% Klason and 2.1% acid-soluble lignin or a total of 24.8%. Klason and acid-soluble lignin values for the reacted woods and the residual reacted woods are given in Table III. In addition, the lignin contents of the reacted woods were estimated by the procedure suggested in Progress Report Two in which the lignin content is taken as the sum of the isolated acetone-soluble hololignin and the lignin

remaining in the residual wood. The lignin content of the 6% reacted wood estimated in this manner definitely appears to be low. This seems to be due to much of the lignin extracted with sodium hydroxide being insoluble in acetone.

Analytical data are given in Table IV for the acetone-soluble hololignins and for the 90% acetone-soluble lignin which was purified by dialysis. Also, results for chlorine dioxide consumption tests are included in the table.

Partial chlorine balances were calculated from the data in Tables III and IV, and the results are given in Table V. For these calculations, it was assumed that all of the sodium hydroxide added to the original chlorine dioxide solutions was converted to sodium chloride. The results show that roughly 40 to 50% of the chlorine was unaccounted for. Part of this was in fractions which were not analyzed, and part probably was lost as hydrogen chloride. The chlorine content of the reacted wood is reduced by alkaline extraction due to removal of chlorinated lignin, but apparently not by alkaline hydrolysis at room temperature.

TABLE V

CHLORINE BALANCE

(Expressed as percentage of available chlorine)

	6% ClO_2	9% ClO_2	18% ClO_2
Acetone-soluble lignin from liquor	10	11	9
Reacted wood	21	16	9
Sodium chloride	32	32	31
Unaccounted for	37	41	51
Acetone-sol. lignin from reacted wood	11	15	7
Residual reacted wood	6	3	2

As discussed in Progress Report Two, it seems useful to compare the various hololignins with each other and with the original lignin by comparing the ratios of the different substituent groups to a hypothetical nonmethoxyl C-9 unit (i.e., to each 9 nonmethoxyl carbons). Choice of the C-9 unit does not imply either that the isolated hololignins are homogeneous or that they actually contain C-9 units. With these limitations in mind, the calculated values are presented in Table VI. The values for hydrogen are for total hydrogen, and are not corrected for the two additional hydrogens due to methoxyl as was done previously. Values for the original aspen lignin were calculated from analytical data for isolated native lignin (6) and for milled wood lignin (2).

For the lignin from the 6% reacted wood which had been purified by dialysis, there was little or no loss of methoxyl, but there was some chlorination and oxidation to acidic groups. In addition, there seemed to be an increase in nonmethoxyl, noncarboxyl hydrogen and oxygen, which could occur by hydrolysis.

On the average, the lignin isolated from the 9% reacted wood had lost 10-20% of the original methoxyl, and had been chlorinated and oxidized to a slightly greater extent than had the dialyzed lignin. About 70% of the methoxyl had been lost in the hololignin isolated from the 9% liquor. Also, this lignin had been chlorinated and oxidized to a considerable extent.

Part of the carbon in the hololignins is present in methoxyl and carboxyl groups, but most is present in other groupings. These other carbons are substituted to varying degrees. Estimates are given in Table VI for the average degree to which each nonmethoxyl, noncarboxyl carbon is substituted by methoxyl, nonmethoxyl hydrogen, and chlorine. These estimates include substitution due to carboxyl and hydroxyl because each of these groups contain one hydrogen and thus are combined with the values calculated for hydrogen.

TABLE VI

CALCULATED VALUES

	Dialyzed Lignin from 9% Reacted Wood	Hololignin from 9% Reacted Wood	Hololignin from 9% Liquor	Original Aspen Lignin
C-9 Unit weight	226	230	304	194-204
Methoxyl/C-9	1.4	1.1	0.4	1.2-1.4
Hydrogen/C-9	13.1	12.4	12.0	11.4-12.0
Oxygen/C-9	4.8	5.2	7.7	3.7-4.2
Chlorine/C-9	0.20	0.32	1.4	--
Carboxyl/C-9[a]	0.22-0.29	0.41-0.57	1.5-2.0	--
Non-MeO, non-COOH oxygen/C-9	2.8-3.0	3.0-3.3	3.3-4.3	2.5-2.8
Substitution/non-MeO, non-COOH carbon[b]	1.2	1.2	1.7-1.8	1.0

[a] The lower value is based on Acid No. II, and the higher on Acid No. I plus Acid No. II.

[b] $\frac{(MeO/C\text{-}9) + [H/C\text{-}9) - 3(MeO/C\text{-}9)] + (Cl/C\text{-}9)}{9 - (COOH/C\text{-}9)}$.

For a long-chain polymer comprised of C_6-C_3 (C-9) units, the average degree of substitution calculated in this manner would approach 1.1 if the end groups were insignificant, and if there were no ethylene or carbonyl groups present. Cross-linking between each unit would reduce this value to 1.0. In a similar polymer which did not contain aromatic groups, the degree of substitution would be 2.0. The increased substitution in the hololignins is believed to be due to destruction of aromatic groups, and to chain and cross-link splitting.

On standing for about 3 months, the ether-soluble fraction from the 9% chlorine dioxide liquor deposited a small amount of needlelike crystals. In an

attempt to identify the crystals, they were subjected to gas chromatography using a FFAP column (Varian Aerograph) with temperature programming to 225°C. A sample of the total ether-soluble material from the 18% chlorine dioxide liquor, and three knowns (vanillin, 5-chlorovanillin, and 6-chlorovanillin) were run in the same manner. The results indicated that the main constituents in both the needles and the total fraction from the 18% liquor were not eluted from the column, and thus were not any of the knowns tested. All samples including the knowns contained two or more minor constituents, and at least one of these seemed to be present in all five samples. Because the ether-soluble fractions represent only a small proportion of the degraded lignins, no further work was done with them.

HOLOLIGNINS FROM PINEWOOD

It is well known that lignins in hardwoods differ considerably from those in softwoods, and hence it was of interest to isolate hololignins from the latter. Southern pine was selected for this purpose. Ordinary chips were hand sorted to remove dirt and fines, and the larger chips were split until the maximum chip size was about 27 x 7 x 4 mm. The selected chips were extracted with acetone to remove extractives, and then were treated with acidified chlorite equivalent to 18% chlorine dioxide at 40 to 55°C. until the oxidant was exhausted.

Acetone-soluble hololignin was isolated from the reacted wood in the usual manner, and a part of this was purified by adding an acetone solution to absolute ether. The yield of the ether-insoluble fraction was 4.4% based on the original wood, or about half that of the total acetone-soluble fraction. Other yields and some analytical data are given in Table VII. Absorptivities for both the total acetone-soluble hololignin, and the ether-insoluble fraction are reported in Table VIII.

TABLE VII

CHLORITE TREATMENT OF PINEWOOD

Yields[a]	
Acetone-soluble extractives, %	1.3
Reacted wood, %	96.5
Acetone-soluble holoLignin, %	8.5
Residual reacted wood, %	87.5
Analytical data for ether-insoluble, acetone-soluble holoLignin[b]	
Chlorine, %	3.8
Methoxyl, %	8.1
Analytical data for residual reacted wood[b]	
Total chlorine, %	1.3
Water-soluble chlorides, %	0.2
Klason lignin, %	12.4
Acid-soluble lignin, %	4.0
Klason + acid-sol. lignin, %	16.4
Modified lignin content of reacted wood[c], %	23.7

[a] Based on the original unextracted wood.

[b] Based on the sample analyzed.

[c] (Acetone-soluble holoLignin isolated from reacted wood) + (Klason and acid-soluble lignin in residual reacted wood), both based on reacted wood.

TABLE VIII

ABSORPTIVITY OF PINE HOLOLIGNINS

λ, nm.	Acetone-Soluble Hololignin, a	Ether-Insoluble Hololignin, a
206	101	97
208	92	89
210	82	80
212	74	72
220	54	50
230	42	38
240	22	22
250	14	15
260	16	15
270	16	15
280	16	16
290	12	14
300	8.1	8.2

The data in Table VII suggest that less than 10% of the original lignin in the pinewood was dissolved by the chlorite treatment, and that more than half of the lignin in the reacted wood was resistant to alkaline extraction. However, at least a part of the lignin in the reacted wood had lost considerable methoxyl and had been chlorinated to some extent. In spite of the loss of methoxyl, the absorptivities of the isolated hololignins were higher than those of aspen hololignins isolated previously. The high absorptivities of the pine hololignins suggest that these products had lost but little of the original aromatic character.

DISCUSSION

In Progress Report Two, it was postulated that the reaction of chlorine dioxide with aspenwood converts the original lignin to a wide series of degradation products ranging from lignins which are modified only slightly to products which are degraded sufficiently to be soluble in the spent liquor. It now appears that the relative proportion of the various degraded lignins depends on the reaction conditions, especially on the amount of chlorine dioxide used. Since neither the conditions for holopulping nor for the isolation of hololignins have been standardized, the results which have been obtained cannot be applied universally. However, some broad generalizations seem justified.

Although the isolations are not entirely satisfactory, it has been possible to recover roughly half to two thirds of the total hololignins as acetone-soluble fractions which seem to be essentially free of nonlignin materials. These isolated materials are mixtures which can be fractionated further, but it is not likely that individual lignins of constant composition can be obtained. Some of the lignin in the reacted wood cannot be extracted with alkali, and hence cannot be studied directly. In addition, some of the extracted lignins are not soluble in dry acetone and are not separated easily from nonlignin materials. Part of these can be separated from sodium chloride by dialysis but part pass through the dialysis membrane along with the salt. These acetone-insoluble fractions also may be contaminated with carbohydrate materials. Gel filtration should be useful for the separation and for fractionation of the recovered hololignins, but this has not been tested as yet.

Previously, secondary reactions seemed to occur when hololignins were isolated from spent chlorite liquors. This was believed to be due to the presence of chlorates in the spent liquor. It now seems that hololignins can be isolated from

spent chlorine dioxide liquors without the occurrence of secondary reactions. Consequently, it is desirable to use chlorine dioxide rather than acid chlorite if hololignins are to be isolated from the spent liquor.

When aspenwood is treated with acidified chlorite equivalent to about 110% chlorine dioxide at 50-55°C. (as in Fig. 1 or as in the preparation of Pulp-4 in Progress Report Two), 50 hours or more are required for exhaustion of the oxidant. Under these conditions the yields were 66% and less, indicating an appreciable loss of carbohydrate materials in the spent liquors. In both cases, analysis indicated that the reacted wood still contained about 0.5% acid-soluble lignin. Extraction with 0.5N sodium hydroxide at room temperature removed 1-1.5% ether- or acetone-soluble materials which apparently consisted of degraded lignins. Hot alkali extracted much more ether- or acetone-soluble materials, but these appear to be of nonlignin origin. They are believed to be due to degradation of some carbohydrates by the extended chlorite treatment. Such materials probably are not formed under the normal holopulping conditions, but this has not been demonstrated as yet.

When aspen chips are treated with 18% or less chlorine dioxide (or the equivalent amount of acidified chlorite) only the outside of the chips is softened sufficiently to be defibered by mild mechanical action. The results indicate that lignin in the interior of the chips may be degraded to a considerable degree without breaking the bonds which hold the fibers together in wood. Unfortunately, the nature of the reactions responsible for defiberization as well as those responsible for delignification are far from clear.

When fiberized aspenwood was treated with 6 or 9% chlorine dioxide, roughly 20% of the original lignin dissolved in the chlorine dioxide liquor, but very little of this had been degraded sufficiently to be soluble in ether. Somewhat more lignin

had been modified to a form which could be extracted with sodium hydroxide; however, much of the lignin had not been changed sufficiently to be extractable with alkali at room temperature. This suggests that one of the chief functions of chlorine dioxide may be to convert the lignin to a form that can be extracted in a second stage. This is in agreement with the early work with chlorine dioxide in which a series of alternate oxidation and extraction stages were used to delignify wood (7,8,9). In any practical holopulping process, it is necessary to limit both the amount of chlorine dioxide and the number of stages. From the data in Table III, it is estimated that the total lignin removed in the combined oxidation and extraction stages was 14.7, 17.9, and 20.0% for the reactions with 6, 9, and 18% chlorine dioxide, respectively. These values are based on the original wood, and indicate lignin removals of 240, 200, and 110% based on the chlorine dioxide used.

The main part of the degraded lignins dissolved in the spent chlorine dioxide liquors were relatively unreactive to chlorine dioxide, possibly because of a rather high degree of chlorination. This is fortunate from the standpoint of optimum use of chlorine dioxide.

The isolated hololignins have been characterized by chemical analysis. Since the isolated fractions consist of mixtures of degraded lignins, the characterizations represent only the average composition. The results indicate clearly that the reaction of chlorine dioxide with aspenwood results in chlorination, demethoxylation, and oxidation of the lignin. For a better characterization, a further fractionation into fractions of more uniform composition is desirable. Molecular weight studies on the isolated lignins should be worthwhile. In addition, there are many possibilities for further characterization by means of various chemical reactions.

The procedure suggested in Report Two for estimating lignin in holopulps may be useful for some holopulps, but it is not very satisfactory when the yield of the chlorine dioxide-reacted wood is about 90% or higher. Under these conditions, an appreciable part of the lignin extracted with sodium hydroxide is not soluble in dry acetone, and this is not included in the estimation.

The work with pine hololignin was only preliminary in nature, and the results are not directly comparable with those obtained for aspen hololignin. However, it seems that the procedures which have been applied to aspen can be used to isolate and characterize pine hololignins.

CONCLUSIONS

1. When aspenwood is reacted with 6 to 18% chlorine dioxide:
   a. the lignin is chlorinated, demethoxylated, and oxidized to varying degrees;
   b. these reactions occur within the center of the chips, but not to an extent sufficient for delignification and defiberization;
   c. relatively little lignin dissolves in the chlorine dioxide liquor; and
   d. much of the lignin remaining in the reacted wood is modified to a form that can be removed by alkaline extraction.
2. The procedure suggested previously for estimating lignin in holopulps is not satisfactory when less than about 9% chlorine dioxide is used to produce the pulp.
3. Hololignins from pinewood can be isolated and characterized by the procedures used for aspen hololignins.

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M. A. Buchanan
Senior Research Associate
Carbohydrate Chemistry Group
Organic Chemistry Section